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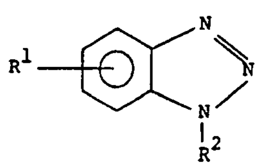
(54) Antimicrobial fibers containing a discoloration inhibitor

(57) Antimicrobial fibers having a silver-containing inorganic microbiocide are obtained by using a treating solution for producing said fibers which contains a discoloration inhibitor represented by the following general formula:



wherein
R^1 is hydrogen or a lower alkyl group and R^2 is hydrogen or an alkali metal.

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PROCESS FOR PRODUCING ANTIMICROBIAL FIBER

The present invention relates to a process for the production of an antimicrobial fiber having a silver-containing inorganic microbiocide, and more particularly but not exclusively, to a process for the production of an antimicrobial fiber which causes no discoloration during or after its treatment step(s) wherein the antimicrobial fiber is treated with treatment solution(s).

The antimicrobial fiber obtained using the present process has no discoloration due to the use of treatment solutions either during or after its production and is an excellent microbiocide. The fiber is therefore useful not only as a single fiber but also in the form of a material for various fiber products such as clothing (e.g. socks, stockings and underwear), bedding (e.g. bedcover and sheet), protective articles (e.g. mask and bandage) and the like.

A number of microbiocides have been proposed which can exhibit antimicrobial properties when incorporated in fibers, coatings, shaped resin articles, papers, binders, etc. Among them, inorganic microbiocides have drawn special attention in recent years, because of their excellent durability.

Most of the inorganic microbiocides are microbiocides obtained by supporting a silver ion, as a component for antimicrobial properties, on an inorganic compound by various methods (these inorganic microbiocides are hereinafter referred to simply as microbiocides). The inorganic compounds on which the silver ion can be supported, include, for example, active carbon, apatite, zeolite and phosphates.

A fiber having a microbiocide (this fiber is hereinafter referred to as an antimicrobial fiber) is subjected, during its spinning process, to various treatment steps such as drawing, scouring, dyeing, bleaching, mixed fiber spinning, weight reduction and the like, and is treated with various treatment

solutions such as textile oils, aqueous alkali solutions, bleaching agents, detergents and the like. During such treatment, the silver ion contained in the microbiocide dissolves in a very small amount in the treatment solutions or reacts with certain components of the treatment solutions, whereby the antimicrobial fiber becomes discolored.

In order to prevent a microbiocide-containing resin from being discolored, it has been proposed to add a stabilizer to the resin so that the resin contains both a microbiocide and a stabilizer. Examples of stabilizers for antimicrobial resin compositions, each comprising (a) an antimicrobial zeolite having a silver ion supported thereon and (b) a resin, are benzotriazole compounds, oxalic acid anilide compounds, salicylic acid compounds, hindered amine compounds and hindered phenol compounds (Japanese Patent Kokai No. 63-265958).

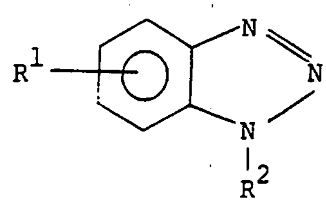
However, when each of these stabilizers is added to a resin for fiber production and the resin is spun into an antimicrobial fiber, it is still impossible to suppress the discoloration of the antimicrobial fiber sufficiently when the antimicrobial fiber is treated with various treatment solutions in the treatment steps or when the spinning solution used for production of the antimicrobial fiber contains a large amount of a solvent. Hence, it has been desired to develop a process for producing an antimicrobial fiber which does not discolour in the various fiber treatment steps.

We have now found it possible to provide a process for producing an antimicrobial fiber having a microbiocide and having excellent antimicrobial properties, which fiber has, during or after production, substantially no discoloration induced by use of treatment solutions or by the spinning solution per se.

The present inventors did extensive research in order to achieve the above task and found that the addition of a

discoloration inhibitor comprising a particular compound to various treatment solutions is very effective.

According to the present invention there is provided a process for the production of an antimicrobial fiber having a silver-containing inorganic microbiocide wherein said process comprises using a treatment solution for producing said fiber which treatment solution comprises a discoloration inhibitor having the following general formula:



wherein R^1 is hydrogen or a lower alkyl group and R^2 is hydrogen or an alkali metal.

Various preferred features and embodiments of the present invention will now be described by way of non-limiting example.

[Raw materials for the antimicrobial fiber]

❒ Base fiber

The base fiber used in the present invention can be any natural or chemical fiber. The natural fiber include, for example, vegetable fibers such as cotton, hemp, flax, coconut, rush and the like; animal fibers such as wool, goat hair, mohair, cashmere, camel hair, silk and the like; and mineral fibers such as asbestos and the like. The chemical fiber includes, for example, inorganic fibers such as rock fiber, metal fiber, graphite fiber, silica fiber, titanate fiber and the like; cellulose fibers such as viscose fiber, cuprammonium fiber and the like; protein fibers such as casein fiber, soybean fiber and the like; regenerated or semi-synthetic fibers such as regenerated silk yarn, alginate fiber and the like; and synthetic fibers such as polyamide fiber, polyester fiber, polyvinyl fiber, polyacrylic fiber, polyurethane fiber, polyethylene fiber, polyvinylidene fiber, polystyrene fiber and the like.

1 ▯ Microbiocide

The microbiocide used in the present invention can be any inorganic compound having a silver ion supported thereon. The inorganic compounds on which silver ion can be supported, include the following, for example: inorganic adsorbents such as active carbon, active alumina, silica gel and the like; and inorganic ion exchangers such as zeolite, hydroxyapatite, zirconium phosphate, titanium phosphate, potassium titanate, antimony oxide hydrate, bismuth oxide hydrate, zirconium oxide hydrate, hydrotalcite and the like.

The method for supporting silver ion on such an inorganic compound is not restricted. There are various specific methods for supporting, such as (1) a method using physical or chemical adsorption, (2) a method using an ion exchange reaction, (3) a method using a binder, (4) a method comprising striking a silver compound into an inorganic compound, and (5) a method which forms a thin layer of a silver compound on the surface of an inorganic compound by a thin-film formation technique such as vapor deposition, dissolution and precipitation, sputtering or the like.

Among the above-mentioned inorganic compounds, inorganic ion exchangers are preferable because a silver ion is fixed thereon strongly. Among the inorganic ion exchangers, particularly preferable is a tetravalent-metal phosphate represented by the following general

formula [1]:

$$M^1_a M^2_2 (PO^4)_3 \cdot nH_2O \quad [1]$$

wherein M^1 is at least one ion having a valency of m, selected from alkali metal ions, alkaline earth metal ions, an ammonium ion and a hydrogen ion; M^2 is a tetravalent metal such as Ti, Zr, Sn or the like; n is a number satisfying $0 \leq n \leq 6$; and a is a positive number satisfying ma=1.

The tetravalent-metal phosphate is a crystalline compound belonging to the space group R3c, and the constituent ions form a three-dimensional network structure.

In the present invention, the microbiocide is preferably one, which is obtained by supporting silver ions on a tetravalent-metal phosphate represented by the general formula [1] and, which is represented by the following general formula [2]:

$$Ag_p M^1_q M^2_2 (PO_4)_3 \cdot nH_2O \quad [2]$$

wherein M^1, M^2 and n are the same as defined above; p and q are positive numbers satisfying p+mq=1 (m is the valency of M^1).

Specific examples of the microbiocide sented by the general formula [2] are shown below.

$Ag_{0.005}Li_{0.995}Zr_2(PO_4)_3$

$Ag_{0.01}(NH_4)_{0.99}Zr_2(PO_4)_3$

$Ag_{0.05}Na_{0.95}Zr_2(PO_4)_3$

$Ag_{0.2}K_{0.8}Ti_2(PO_4)_3$

$Ag_{0.1}H_{0.9}Zr_2(PO_4)_3$

$Ag_{0.05}H_{0.05}Na_{0.90}Zr_2(PO_4)_3$

$Ag_{0.20}H_{0.20}Na_{0.60}Zr_2(PO_4)_3$

$Ag_{0.05}H_{0.55}Na_{0.40}Zr_2(PO_4)_3$

A fiber having a microbiocide of the general formula [2] causes only slight discoloration when treated with the various treatment solutions mentioned later but, when said treatment solutions or the spinning solution of said fiber contain a discoloration inhibitor of the present invention, surprisingly causes no discoloration results.

The tetravalent-metal phosphate can be synthesized by a firing process, a wet process, a hydrothermal process, etc. For example, a tetravalent-metal phosphate wherein the tetravalent metal is zirconium, can be easily obtained as follows by a wet process.

Oxalic acid and phosphoric acid are added, in this order, to an aqueous solution of zirconium oxynitrate and sodium nitrate, with stirring. The mixture is adjusted to pH 3.5 with an aqueous sodium hydroxide solution and then refluxed under heating for 78 hours.

The resulting precipitate is collected by filtration, water-washed, dried and disintegrated to obtain zirconium phosphate [$NaZr_2(PO_4)_3$] having a network structure.

The zirconium phosphate is immersed in an aqueous solution containing an appropriate concentration of silver ions, whereby a microbiocide of the general formula [2] is obtained.

In order to obtain a microbiocide of the general formula [2] having high antifungal, antibacterial and antialgal properties, p in the general formula [2] is desirably large. However, when p is 0.001 or larger, sufficient antifungal, antibacterial and antialgal properties can be obtained. When p is smaller than 0.001, it may be difficult to obtain antifungal, antibacterial and antialgal properties over a long period of time. In view of this and economy, p is preferably in the range of 0.01-0.5.

An antimicrobial fiber can be obtained by supporting the above-mentioned microbiocide on or in the above-mentioned base fiber. The method for supporting has no particular restriction. The supporting method can be exemplified by a method which comprises kneading a resin to be made into the fiber and a microbiocide and subjecting the mixture to spinning, and a method which comprises applying a microbiocide mixed with a binder, to the surface of a spun fiber by coating, dipping or the like.

[Treatment solutions]

The treatment solutions used in the present process refer to those which are used for producing an antimicrobial fiber in the spinning step to the finishing step of fiber production, and which contain a particular discoloration inhibitor represented by the general formula [3] shown later.

Incidentally, the antimicrobial fiber of the present invention refers not only to a fiber obtained by a spinning step but also to a fiber precursor immediately after being taken out of a spinning nozzle.

Each of the treatment solutions used in the present process can contain various components conventionally used for the efficient operation of each treatment step.

The treatment steps actually employed are appropriately selected depending upon the kind of fiber to be produced. They include, for example, a spinning step, a cotton spinning step, a silk reeling step, a wool scouring step, a drawing step, a decolorization step, a twisting step, a cutting step, a washing step, a weaving and knitting step, a bleaching step, a dyeing step, a sizing and desizing step, a printing step, a dyeing-by-dipping step and a weight reduction step.

The treatment solutions typically used in these treating steps are an oil for spinning or weaving, a detergent, a dyeing assistant, a finishing agent and an aqueous alkali solution used in the weight reduction step. Specific examples thereof are as follows:

the oil for spinning or weaving includes an oil for a chemical fiber, an oil for worsted spinning, an oil for woollen spinning, an oil for hard and bast fiber spinning, an oil for synthetic fiber spinning, a sizing agent and oil for hank yarn, a sizing agent and oil, an oil for general fabric, an oil for silk yarn spinning, etc. The detergent includes a desizing

assistant and detergent for cotton, a detergent for grease wool, an unwinding agent for cocoon, a bleaching assistant, a mercerization assistant, an assistant for carpet weaving, a degreasing agent for grease wool, a desizing and detergent for staple fiber, silk, hemp or a synthetic fiber, etc. The dyeing assistant includes a dyeing assistant for wool, a dyeing assistant for cotton or a staple fiber, a dyeing assistant for acetate, a dyeing assistant for polyamide fiber, a dyeing assistant for polyacrylic (mixed) fiber, a dyeing assistant for polyester (mixed) fiber, a printing assistant, etc. The finishing agent includes a softening agent for synthetic fiber or mixed fiber, a resin finishing agent, an agent for water resistance or oil resistance, an antistatic agent, etc.

Each of these treatment solutions is ordinarily a mixture of components including a surfactant and/or an alkaline compound. Typical examples of the components are as follows.

(Alkaline compound): sodium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, sodium sesquicarbonate, soda ash, sodium silicate, slaked lime, ammonia water, etc.

(Organic solvent): benzene, kerosene, naphtha, etc.

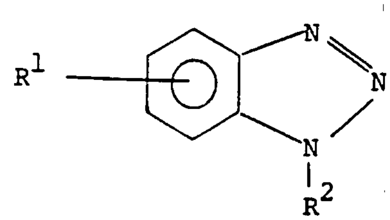
(Soap): soaps such as laurate, myristate, palmitate, stearate, oleate soaps and the like; solvent-containing soaps; organic base soaps such as ethanolamine soap, cyclohexylamine soap, alkylamine soap and the like; and so forth.

(Dispersant or surfactant): alkylaryl sulfonation products and higher sulfonic acid oils; alkylsulfonic acids, olefinsulfonic acids, alkylbenzenesulfonic acids, naphthalenesulfonic acid and salts thereof; alkyl ether sulfates, alkylamide sulfates, sulfonated oils, vegetable oil sulfates, higher aliphatic alcohol sulfates and salts of higher alcohol sulfates; condensation products of fatty acids; proteins and aliphatic condensation products; salts of phosphoric acid esters, such as salts of alkyl phosphates, salts of alkyl ether phosphates and the like; acylated peptides and carboxylic acid salts such as salts of alkyl ether carboxylates and the like; aliphatic amine salts, aliphatic quaternary ammonium salts, aromatic quaternary ammonium salts and heterocyclic quaternary ammonium salts; imidazoline derivatives, aminocarboxylic acid salts and betaine; ethylene oxide condensation products, condensation products between oleic acid and aminosulfonic acid and condensation products between fatty acids and proteins; and so forth.

(Reducing agent): sulfurous acid gas, sodium sulfite, zinc powder, Candit V, grape sugar, etc.
(Oxidizing agent): aqueous hydrogen peroxide solution, sodium peroxide, sodium hypochlorite, potassium permanganate, chrolamine TO, etc.
(Enzyme): animal enzymes such as pancreatin, trypsin, Fermasol and the like; and vegetable enzymes such as malt enzymes (e.g., Amiladine, Brimal and Dextose) and bacterial enzymes (e.g., Biolase and Rapidase).
(Others): higher alcohols, animal or vegetable waxes, mineral waxes, vegetable oils, mineral oils, methyl esters of vegetable oils, liquid paraffin, etc.

□ Discoloration inhibitor

The discoloration inhibitor used in the present process is a compound represented by the following general formula [3]



[3]

wherein R^1 is hydrogen or a lower alkyl group and R^2 is hydrogen or an alkali metal.

When R^1 is a lower alkyl group, the lower alkyl group is preferably methyl, ethyl, n-propyl, isopropyl and butyl. Methyl is particularly preferable because the compound of the general formula [3] wherein

R^1 is methyl, has high stability.

When R^2 is an alkali metal, the alkali metal is preferably lithium, sodium, potassium and cesium.

Preferable examples of the compound of the general formula [3] are methylbenzotriazole and the potassium salt thereof.

Benzotriazole type compounds have been known as a resin stabilizer. In the present invention it has been found that when, among various benzotriazole type compounds, any of the above particular compounds of the general formula [3] are added to a treatment solution for a fiber and the resulting treatment solution is used for treatment of an antimicrobial fiber having a silver ion-containing microbiocide, the antimicrobial fiber after the treatment has substantially no discoloration; this is surprising.

The amount of the discoloration inhibitor used in the treatment solution is preferably 0.005-5 parts by weight (parts by weight are hereinafter referred to simply as parts), more preferably 0.05-0.5 part per 100 parts of the treatment solution. When the amount is smaller than 0.005 part, it may be difficult to sufficiently suppress the discoloration of the antimicrobial fiber. Meanwhile, when the amount is larger than 5 parts, there is seen substantially no higher effect on suppression of discoloration and rather such an amount may give an unfavorable influence on the expected effect of each treating solution.

The discoloration inhibitor of the present invention can exhibit an especially striking effect when used in a treatment solution containing a surfactant and/or an alkaline compound in a high concentration, for example, an oil for spinning or an alkaline detergent.

□ Preparation of treatment solutions

Each of the treatment solutions used in the present process can be easily prepared by mixing or kneading the above discoloration inhibitor (a benzotriazole type compound) with a treatment solution under a temperature and a pressure appropriately selected (if necessary, heating and increasing or decreasing of pressure are employed) in view of the properties of the fiber to be treated. The specific operations for the above preparation can be conducted in an ordinary manner.

The benzotriazole type compounds used in the present process include hydrophilic ones and oleophilic ones. Hence, a benzotriazole type compound highly soluble or dispersible in the treating solution to be used must be appropriately selected in order to obtain a sufficient effect for suppression of discoloration.

In preparing a treatment solution used in the present process, a discoloration inhibitor of the present invention is incorporated at an appropriate concentration in a conventional treatment solution (composition) such as an oil for spinning, a mercerization assistant, a finishing agent or the like. Examples of such formula-

tions are shown below. (In the followings, R is an alkyl group; n is a positive number; and each amount used refers to parts by weight.)

(Oil for spinning)

		Parts used
1.	Ultrafine particle colloidal silica	100
	$RN^+[(C_2H_4O)_nH]_2CH_2COO^-$	50
	Benzotriazole type compound (discoloration inhibitor)	2.0
2.	$R{-}O(CH_2CH_2O)_nH$	100
	$R{-}OSO_3Na$	35
	$R{-}COOR(OH)_2$	25
	Higher alcohol	10
	Mineral oil	10
	Benzotriazole type compound (discoloration inhibitor)	1
	Water	50
3.	Esterified oil	100
	Liquid paraffin	60
	$R{-}O(CH_2CH_2O)_nH$	40
	Benzotriazole type compound (discoloration inhibitor)	0.6

(Sizing agent and oil)

4.	Aqueous polyacrylic acid solution	100
	Benzotriazole type compound (discoloration inhibitor)	0.3
5.	$RO(C_2H_4O)_nH$ sulfonated sperm oil	30
	Neutral paraffin wax	100
	Benzotriazole type compound (discoloration inhibitor)	0.3

(Marcerization assistant)

6.	25° Be′ sodium hydroxide	100
	$ROSO_3Na$	0.15
	Benzotriazole type compound (discoloration inhibitor)	0.3
	Water	0.35

(Washing agent for woolen cloth)

7.	$R-C_6H_{10}O-(C_2H_4O)_nH$	0.1
	Higher alcohol detergent	0.2
	Soda ash	0.1
	Benzotriazole type compound (discoloration inhibitor)	0.4
	Water	100

(Dyeing assistant)

8.	$ROSO_3Na$	15
	Dichlorobenzene	100
	Benzotriazole type compound (discoloration inhibitor)	0.5
	Water	40

(Finishing oil agent)

9.	Lanolin	50
	$RCOO(CH_2CH_2O)_nH$	100
	Polyamine derivative	70
	Benzotriazole type compound (discoloration inhibitor)	1.5

(Antistatic agent)

10.	Salt of alkyl phosphate	100
	Benzotriazole type compound (discoloration inhibitor)	0.5

[Preparation of antimicrobial fiber]

In producing an antimicrobial fiber according to the present process, there is no restriction to the spinning method, and a spinning method suitable for the specific fiber to be produced can be appropriately selected from conventional spinning methods, i.e. basic spinning methods (e.g. melt spinning, wet spinning and dry spinning), an emulsion spinning method, a conjugate spinning method, spinning methods using no spinning nozzle (e.g., a spinning method comprising cutting of drawn thin film, drawing and heat setting, spinning method by drawing of a rod-like

polymer, and a spinning method by interfacial polymerization), and the like.

When a polymer material already containing a microbiocide is subjected to wet spinning (in this case, said polymer material is dissolved in a solvent and the solution is used as a spinning solution) or to dry spinning, there is a high risk of microbiocide discoloration. In order to prevent it, the spinning solution can contain a discoloration inhibitor of the present invention.

As previously mentioned, the amount of the discoloration inhibitor of the general formula [3] used in the treatment solution is preferably 0.005-5 parts, more preferably 0.05-0.5 parts per 100 parts of the treating solution. When the amount is smaller than 0.005 part, it may be impossible to sufficiently suppress the discoloration of the antimicrobial fiber. Meanwhile, when the amount is larger than 5 parts, there is seen substantially no higher effect on suppression of discoloration, and rather such an amount may give an unfavorable influence on the expected effect of each treatment solution.

In treating an antimicrobial fiber with a treatment solution containing a particular discoloration inhibitor according to the present process, there is no particular restriction to the treatment, and the treatment can be conducted in the same manner as in the treatment steps conventionally used in fiber production.

A treatment solution containing a discoloration

inhibitor gives no unfavorable influence on the antimicrobial fiber to be produced, during and even after fiber production. It is therefore not necessary to completely remove, by washing, the treatment solution remaining on the fiber. Rather, the presence of a small amount of the discoloration inhibitor on the surface of the antimicrobial fiber can effectively prevent the possible discoloration of the antimicrobial fiber due to its contact with a discoloration-inducing substance or the like.

According to the process of the present invention, the antimicrobial fiber having a silver ion-containing microbicide has no discoloration due to use of various treatment solutions during fiber production; and further the antimicrobial fiber after the treatment has no discoloration over a long period of time even in a severe environment and maintains antifungal, antibacterial and antialgal properties.

[Applications]

The antimicrobial fiber obtained by the present process, having excellent antimicrobial properties and moreover being free from discoloration, can be used widely in various applications. It has a particular advantage of maintaining whiteness and cleanness and can be used, for example, in the following specific applications: clothing such as socks, stockings, underwear and the like; bedding such as bedcover, sheet and the like; protective articles such as mask, bandage

and the like; textile products such as towel and the like; hairs for brushes; fishing nets; and so forth.

The present invention is described in more detail below with reference to the following non-limiting Examples.

Example 1 [Preparation of microbiocides]

An aqueous zirconium sulfate solution and an aqueous sodium dihydrogenphosphate solution were mixed so as to give a ratio of zirconium to phosphorus of 2:3, whereby a precipitate was formed. The mixture was adjusted to pH 2 with an aqueous sodium hydroxide solution and then placed in a hydrothermal state at 150°C for 24 hours, whereby crystalline zirconium phosphate was obtained.

The zirconium phosphate was added to an aqueous solution of silver nitrate and nitric acid. The mixture was stirred at room temperature for 4 hours, then washed with water thoroughly and dried. The resulting material was fired at 750°C for 4 hours, followed by disintegration to obtain a microbicide "a" as a white powder having an average particle diameter of 0.47 μm.

There was also prepared a microbicide "b" by subjecting a commercial zeolite to the same silver ion exchange. The compositions of the microbiocides a and b are shown in Table 1.

Table 1

Kind of microbicide	Composition
a	$Ag_{0.20}H_{0.20}Na_{0.60}Zr_2(PO_4)_3$
b	$0.03Ag_2O \bullet 0.9Na_2O \bullet Al_2O_3 \bullet 2.0SiO_2$

Example 2 [Preparation of antimicrobial fibers]

A portion of each of the microbiocides a and b obtained in Example 1 was mixed with a nylon 6 resin for fibers. Each of the microbiocide-containing resins was subjected to melt spinning in an ordinary manner to obtain two antimicrobial fibers each of about 90 deniers (24-multifilament). There was also prepared a comparative fiber containing no microbiocide in the same manner.

In Table 2 there are shown the relations of sample Nos. of the resulting antimicrobial and comparative fibers and microbiocides contained therein.

Table 2

Sample No.	Kind of microbicide
1	No microbicide contained
2	a
3	b

Example 1

[Preparation of fiber-treatment solutions]

0.3 part by weight of a discoloration

inhibitor (potassium salt of methylbenzotriazole) was added to 100 parts by weight of an ester type spinning oil or a 10% aqueous sodium hydroxide solution, and they were thoroughly mixed, whereby a discoloration inhibitor-containing spinning oil and a discoloration inhibitor-containing alkali treating solution were prepared.

[Evaluation of discoloration inhibitor-containing spinning oil]

Each of the antimicrobial fibers and microbiocide-free fiber obtained in Example 2 was dipped in the discoloration inhibitor-containing ester type spinning oil and dried, then exposed to sunlight outdoors for 1 day, and visually examined for fiber discoloration.

For comparison, the same procedure was conducted using the ester type spinning oil containing no discoloration inhibitor. The thus obtained effects of the discoloration inhibitor-containing ester type spinning oil and the comparative spinning oil are shown in Table 3.

Table 3

Sample No.	Microbiocide	Effect (color change): Using discoloration inhibitor	Effect (color change): Using no discoloration inhibitor
1	Not used	No discoloration	No discoloration
2	a	No discoloration	Changed to light brown
3	b	No discoloration	Changed to brown

[Evaluation of discoloration inhibitor-containing alkali treating solution]

Each of the antimicrobial fibers and microbiocide-free fiber obtained in Example 2 was dipped in the discoloration inhibitor-containing alkali treating solution in a closed vessel. The closed vessel was kept at 121°C for 10 minutes. Then, each fiber was taken out, washed with water and visually examined for fiber discoloration. For comparison, the same procedure was conducted using the alkali solution containing no discoloration inhibitor. The thus obtained effects of the discoloration inhibitor-containing alkali treating solution and the comparative alkali treating solution are shown in Table 4.

Table 4

Sample No.	Microbiocide	Effect (color change): Using discoloration inhibitor	Effect (color change): Using no discoloration inhibitor
1	Not used	No discoloration	No discoloration
2	a	No discoloration	Changed to light yellow
3	b	No discoloration	Changed to brown

As clear from Table 3 and Table 4, the antimicrobial fibers treated with discoloration inhibitor-containing treating solutions caused no discoloration similarly to the fiber containing no microbiocide The antimicrobial fibers treated with discoloration inhibitor-free solutions caused significant discoloration.

[Test for antimicrobial property]

Each of the sample Nos. 1, 2 and 3 after treatment with the discoloration inhibitor-containing ester type spinning oil or with the discoloration inhibitor-containing alkali treating solution was subjected to the following test for antimicrobial properties.

A 1g sample of each fiber was weighed and cut into small pieces to prepare a sample. The sample was added to 15 ml of a phosphate buffer solution placed in an

Erlenmeyer flask. Thereto was added a solution of Escherichia coli so as to give a concentration of about 10^5 microbes/ml. The mixture was shaked at 27°C for 1 hour. 1 ml of the mixture was taken and cultured at 36°C for 1 day in a standard agar medium by dilution plate culture method, after which the number of living microbes was counted. The results of the test are shown in Table 5.

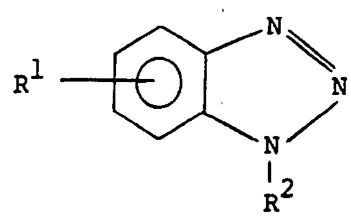
Table 5

Sample No.	Number of living microbes: Ester type oil	Number of living microbes: Alkali treating solution
1	4.5×10^5	5.0×10^5
2	Smaller than 10	Smaller than 10
3	Smaller than 10	3.1×10^2

As clear from Table 5, each of the sample Nos. 2 and 3 each containing a microbiocide showed excellent antimicrobial properties.

CLAIMS

1. A process for the production of an antimicrobial fiber having a silver-containing inorganic microbiocide wherein said process comprises using a treatment solution for producing said fiber which treatment solution comprises a discoloration inhibitor having the following general formula:



wherein R^1 is hydrogen or a lower alkyl group and R^2 is hydrogen or an alkali metal.

2. A process according to claim 1, wherein R^1 is methyl and R^2 is hydrogen or potassium.

3. A process according to claim 1 or claim 2, wherein the treatment solution contains the discoloration inhibitor in an amount of 0.005-5 parts by weight per 100 parts by weight of the treatment solution.

4. A process according to any preceding claim, wherein the silver-containing inorganic microbiocide is an inorganic ion exchanger having a silver ion supported thereon.

5. A process according to claim 4, wherein the silver-containing inorganic microbiocide has the following general formula:

$$Ag_pM^1_qM^2_2(PO_4)_3 \cdot nH_2O$$

wherein M^1 is at least one ion selected from alkali metal ions, alkaline earth metal ions, an ammonium ion and a hydrogen ion; M^2 is a tetravalent metal selected from Ti, Zr and Sn; n is a number satisfying $0 \leq n \leq 6$; and p and q are positive numbers satisfying $p+mq=1$ wherein m is the valency of the ion M^1.

6. A process according to claim 5, wherein p is 0.01 to 0.5.

7. An antimicrobial fiber produced using the process of any preceding claim.

8. An article prepared from the antimicrobial fiber of claim 7.

9. A process according to claim 1 substantially as hereinbefore described.

10. An antimicrobial fiber according to claim 7 substantially as hereinbefore described.

11. An article according to claim 8 substantially as hereinbefore described.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report) 27

Application number
GB 9323650.3

Relevant Technical Fields

(i) UK Cl (Ed.L) A5E ET EN

(ii) Int Cl (Ed.5) A01N 25/00

Search Examiner
P N DAVEY

Date of completion of Search
4 JANUARY 1994

Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI

Documents considered relevant following a search in respect of Claims :-
1-11

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).